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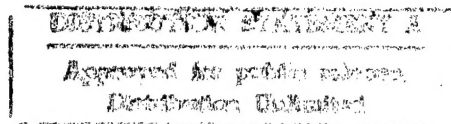
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"Solvation and Ionization of Hydroxyl Groups in
Water-Ice Layers on Silver(110)"

by

D. S.-W. Lim and E. M. Stuve

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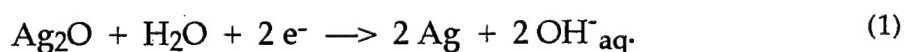
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ABSTRACT

Solvation and ionization of hydroxyl groups on Ag(110) were examined with isotope exchange experiments involving OD and ^{18}OD , and temperature programmed desorption (TPD). Water adsorption onto oxygen-covered Ag(110) gives rise to the well known α , β , γ , and δ peaks in TPD. The α state represents multilayer water, the γ state an $(\text{OH})\cdot\text{H}_2\text{O}$ complex, and the δ state OH groups. The identity of the β state is the subject of this paper. Surface solvation of OH groups involves as many as 17 water molecules (β and γ) in the limit of zero OH coverage and decreases linearly to 6 water molecules for 0.16 ML of OH. The solvating molecules are essentially all β -state molecules as the γ -state contains only 0.5 water molecules per OH group. The maximum coverage of solvating water molecules and OH groups is 1.04 ML in good agreement with a perfect bilayer coverage of 1.18 ML on Ag(110). From this we identify the β -state as an extended surface bilayer structure. Isotope exchange experiments demonstrated proton mobility in the OD/ H_2O adlayer at temperatures of 150 K and below as well as migration of ^{18}OD groups from the surface and into α -state, multilayer water molecules. This constitutes desorption of hydroxide ion into the water-ice multilayers; the analogy between this reaction and electrochemical reduction of silver oxide is discussed.

1. Introduction

Interactions between water and hydroxyl are of fundamental interest to areas like electrochemistry, corrosion, and battery technology [1-3]. For example, the cathodic reaction of a zinc/silver oxide battery involves the reaction of water with silver oxide to produce metallic silver and hydroxide ion,



Molecular level details of this reaction (1), and many similar ones, are still not well understood. In this work we study the structure and ionic nature of water-hydroxyl adlayers on Ag (110).

On silver, water dissociates to form OH [4-12] in the presence of adsorbed atomic oxygen at temperatures as low as 80 K:



The results of early isotopic exchange experiments of Bowker et. al. [13] suggested the possible ionic nature of OH species on Ag(110). They observed exchange between a chemisorbed layer of ^{18}O and H_2O stabilized by the chemisorbed oxygen (the β , γ and δ states, see below). Based on results from ultraviolet photoemission spectroscopy, Barteau and Madix [5] also suggested that surface OH groups are ionic. In a study of the reaction of water with *molecular* oxygen on Ag(110), Madix and Roberts [12] reported that water multilayers stabilize O_2 on the surface, shifting its desorption peak from 170 K

to 200 K. The mechanism for this effect was not identified, but it occurs only in the presence of the multilayer (α) state.

Surface adlayers consisting of ionic species like OH⁻ and solvent molecules like water are analogous to the near-surface region of an electrode/electrolyte interface [14]. Ionic species in these electrolytic adlayers can either adsorb specifically on the metal surface or can be fully hydrated, depending on the interactions among the metal substrate, the water molecules and the ionic species. Ion formation in electrolytic adlayers has been observed in several systems under ultra-high vacuum (UHV) conditions: (1) hydronium ion (H₃O⁺) from coadsorbed H and H₂O on Pt(111) [15] and Pt(100) [16], and (2) hydrated perchlorate ion (ClO₄⁻) from coadsorption of ClO₄ and H₂O on Ag(110) [17]. In the H/H₂O/Pt systems, isotope exchange between chemisorbed deuterium and H₂O conclusively proved the existence of hydronium ion, and the presence of a vibrational band at about 1150 cm⁻¹ provided further confirming evidence [15, 16]. In the case of perchlorate, the presence of non-specifically adsorbed ClO₄ was shown by the change in surface symmetry from C_{3v} for adsorbed, anhydrous ClO₄ to T_d for fully hydrated ClO₄ [17].

Energetic considerations are useful in predicting ion solvation. In the H₂O/H and H₂O/ClO₄ examples above, both processes were shown to be energetically favorable, with respective free energy changes of -0.1 eV [16] and -1.3 eV [17]. In the case of H₂O/H/Cu(110), however, the unfavorable free energy change of +3.6 eV and supporting experimental evidence lead to the conclusion that hydronium ions do not form in this case [18, 19].

An alternative method for comparing UHV and electrochemical (EC) reactions is by means of the UHV-EC analogy,

$$\Phi = e (E_{\text{NHE}} + E_k) \quad (3)$$

in which Φ is the work function of the adsorbate covered surface, e the magnitude of the charge of an electron, E_{NHE} the standard reduction potential, and E_k the so-called absolute electrode potential of a normal hydrogen electrode (referenced to a point just outside the surface of the electrolyte) [14,20]. The latter quantity has been reported as 4.4 V [21,22] and 4.8 V [23,24]. Reaction (1) has a standard reduction potential of 0.342 V, meaning that reaction to the right is favored at lower potentials. This standard reduction potential corresponds to work function ranging from 4.7 to 5.1 eV, which are well above that of $\text{H}_2\text{O}/\text{OH}$ on $\text{Ag}(110)$ [14,20]. From the UHV-EC analogy, therefore, one expects that the reaction of water with oxygen on silver will lead to formation of hydroxide ions.

In this paper we report and examine the evidence for solvation and ionization of OH in water adlayers on $\text{Ag}(110)$ under cryogenic, UHV conditions. We first consider the surface solvation number as a function of OH-stabilized, water coverage to propose a possible model of OH- H_2O surface interactions. When OH ions are solvated in the water adlayers, the course of OH- H_2O interactions can be followed by isotopic exchange between labeled OH groups and unlabeled H_2O molecules, as well as the mobility of isotopically labeled species. To test proton exchange, we label the hydroxyl groups as OD, and to test for hydroxyl mobility we label them as ^{18}OD . We

also use a Born-Haber thermodynamic cycle to show the feasibility of OH ionization and solvation in this system.

2. Experimental Procedure

The experiments were carried out in a two-level, stainless-steel UHV chamber with a base pressure of 2×10^{-10} Torr that has been described elsewhere [16,25]. Preparation and characterization of the silver substrate have also been previously reported [26]. Temperature programmed desorption (TPD) measurements were performed with a Balzers QMG 112 mass spectrometer attached to a computer for multiple signal acquisition [27]; the heating rate was 3 K/sec.

Oxygen-16 (Matheson, extra dry) was used as received. Deuterium oxide (Cambridge Isotope Laboratory, 99.9 %) and oxygen-18 (Isotonec, 99.9 %) were used in the isotopic exchange experiments. Water was doubly de-ionized, distilled, and subjected to several freeze-thaw cycles to remove dissolved gases. Oxygen and D₂O exposures were made through separate glass capillary array dosers [28]. The dosing assembly was located about 5 mm from the sample during adsorption. Water vapor (H₂O) was introduced to the crystal directly from a cone-shaped effusive doser [29] located at the upper level of the chamber. Mass spectrometer measurements detected no contamination of the H₂O source by either HDO or D₂O.

To prepare the surface with OD, the silver crystal was sputtered clean with Ar⁺ ions and annealed to 773 K before each set of experiments. The

substrate subsurface region was saturated with oxygen, $^{16}\text{O}_2$, by 8-9 adsorption-desorption cycles. The chemisorbed OD layer was prepared by first exposing the sample to O_2 to produce adsorbed, atomic oxygen at 270 K, and then cooling it to 110 K for D_2O adsorption. Adsorbed D_2O reacts with oxygen to form OD according to equation (2). Next, the sample was annealed to 200 K to remove the low temperature adsorption states of water and to leave only the OD chemisorbed layer on the surface. The experiment continued by cooling the sample back to 110 K to adsorb the H_2O adlayers.

The ^{18}OD chemisorbed layer was prepared in a similar fashion as the OD layer, but $^{18}\text{O}_2$ was used instead of $^{16}\text{O}_2$ for both subsurface saturation and ^{18}OD layer preparation. The ^{18}OD adlayers always contained substantial amounts of ^{16}OD , however. The main source of ^{16}OD came from the reaction of D_2^{16}O with ^{18}O to make the hydroxyl groups. A secondary source of ^{16}O came from subsurface oxygen [30]. Numerous adsorption-desorption cycles of $^{18}\text{O}_2$ were performed to exchange subsurface ^{16}O by ^{18}O , but this exchange could not be completed. For the ^{18}OD experiments reported in this paper the ratio of ^{18}OD : ^{16}OD was approximately 1:3. The presence of ^{16}OD does not affect the conclusion drawn from Figure 4, which is the only use of ^{18}OD results.

Calibration of coverages of oxygen, water and hydroxyl were performed as previously described [4,31]. All coverages are reported in units of monolayer (ML) based on the number of topmost silver atoms of the perfect (110) surface: $8.45 \times 10^{14} \text{ cm}^{-2}$.

3. Results

A typical TPD spectrum for water adsorbed on an oxygen-covered Ag(110) surface is shown in Figure 1. Four desorption states were observed in the water ($m/e = 18$) TPD spectrum in agreement with previous results [4-10]. The α desorption state at 170 K is the multilayer ice state. The β state occurs at 190K, and its structure is one of the subjects of this paper. The γ state at 225 K has been attributed to the formation of an $(OH)_2\text{-H}_2\text{O}$ complex with both water molecules and hydroxyl groups in direct contact with the surface [4,32]. The surface hydroxyl recombination (reverse of reaction (2)) occurs at 300 K and is labeled the δ state.

To probe the H/D exchange of OH in the water adlayers, surface OD groups were prepared and then covered with H_2O adlayers. In the subsequent TPD experiments, we detected both D_2O ($m/e = 20$) and HDO ($m/e = 19$) in all desorption states of water. Figure 2 shows TPD spectra of D_2O following adsorption of H_2O on a surface precovered with 0.12 ML OD. The notation at the top of the figure shows the species detected to the left of the double slash and the preparation of the adlayer (in reverse order) to the right of the double slash. In all cases, the signals of both D_2O and HDO (not shown) were above the background level. At low water coverage no desorption of D_2O was observed in the α state, though the α state did appear for H_2O as shown in Figure 3. The thin line is the spectrum of D_2O and the thick line is that of H_2O . The desorption of D_2O begins to appear in the α state with 0.7 ML of H_2O (Fig. 2) and grows with increasing water coverage. Similar behavior was observed in the TPD spectra of HDO .

The mobility of hydroxyl groups was examined by labeling them as ^{18}OD to follow the migration of both hydrogen and oxygen atoms of ^{18}OD in the H_2O ice layers. We observed the presence of HD^{18}O ($m/e = 21$) in all states of the TPD spectra shown in Figure 4. Desorption of D_2^{18}O ($m/e = 22$) was below the detection limit of our instrument. HD^{18}O desorption in the α state appears for 1.4 ML and 2.5 ML of H_2O coverage, but not for 0.4 ML. Similar to the results of the H/D exchange experiments, we observed an increase in the α state of HD^{18}O with increasing water coverage. Desorption of β and γ states occurs in all cases, though γ state desorption is minimal at 2.5 ML H_2O coverage.

4. Discussion

Surface Solvation Number and OH-Induced Stabilization

On a clean $\text{Ag}(110)$ surface, water desorbs at about 170 K as shown in the α state peak in Figure 1. The presence of co-adsorbed OH, however, stabilizes molecular water and the higher temperature β and γ desorption states occur. Similar stabilization of water on $\text{Ag}(110)$ by coadsorbed model anions has been observed for F [33,34], Cl [25], and Br [7]. A measure to quantify the stabilization of surface water is the surface solvation number N_s given by [33]

$$N_s = \frac{\theta_\beta + \theta_\gamma}{\theta_{\text{OH}}}, \quad (4)$$

where θ_β and θ_γ are the coverages of water in the β and γ states, respectively, and θ_{OH} is the coverage of surface OH. The surface solvation number is the

total amount of water molecules stabilized by each hydroxyl group, which serves as the model anion in this case.

Figure 5 illustrates the dependence of surface solvation number and total coverage of stabilized water θ_w^s , which is equal to the numerator of the right hand side of Eq. (4), on OH coverage. The open squares are the data for solvation number, and the straight line is the best fit line through the data. The filled circles are data for the total coverage of stabilized water, and the curve through those data points is a quadratic function that follows directly from Eq. (4). Both variables are relatively insensitive to the overall coverage of water, which varies between 1 - 2 ML and includes the α state. The surface solvation number decreases linearly from 14 to 5 for OH coverage increasing from 0.05 to 0.15 ML. The extrapolated surface solvation number in the limit of zero OH coverage is 17. High surface solvation numbers have also been observed in coadsorption systems like $\text{H}_2\text{O}/\text{Cl}$ [25] and $\text{H}_2\text{O}/\text{F}$ [33]. At the limit of zero anion coverage, the maximum surface solvation number is 13 in both of those cases. The high surface solvation number of OH at low coverages suggests the formation of either extended surface phases or compressed three-dimensional solvation shells.

The total coverage of stabilized water increases as a function of OH coverage until it reaches a maximum of $\theta_{w,\text{max}}^s = 0.93$ at $\theta_{\text{OH}} = 0.11$ and then decreases at higher OH coverages. Similar relationships between stabilized water and adsorbed anions have been previously observed for $\text{H}_2\text{O}/\text{Cl}$ [25] and $\text{H}_2\text{O}/\text{Br}$ [7]. The increase of stabilized water with coverage of OH suggests that an increasing number of water molecules are being stabilized by surface OH. At the maximum the combined water and OH coverage of 1.04 ML is in

very good agreement with the coverage of a perfect bilayer of 1.18 ML. For comparison the $\text{H}_2\text{O}/\text{Cl}$ coadsorption system also exhibits a maximum coverage of stabilized water of 1.15 ML along with a $c(2\times 2)$ LEED pattern. Adsorbed water in that case forms a bilayer extended along the entire surface, and we propose a similar extended surface bilayer for the $\text{H}_2\text{O}/\text{OH}$ system. Figure 6 shows an approximate view of the extended surface bilayer. This bilayer is optimally developed for an OH coverage of 0.11 ML, which gives the maximum amount of stabilized water. At higher OH coverages, there is a competition for sites between OH and water and the amount of stabilized water decreases.

At the maximum coverage of stabilized water, a surface solvation number of 8 was obtained in our experiments. Gas phase single ion hydration measurements show that the maximum hydration number of $\text{OH}^-_{(\text{g})}$ is 5 [35,36], whereas that of $\text{OH}^-_{(\text{aq})}$ is in the range of 4 - 6.6 [37]. In the $\text{Cl}/\text{H}_2\text{O}$ coadsorption system, however, the surface solvation number is 5 at the maximum stabilized water coverage and the maximum hydration number in single ion gas phase is 4 [33]. In both the OH and Cl cases, the surface solvation numbers at maximum stabilized water coverage are slightly greater than the maximum gas phase hydration numbers. It seems that adsorbed anions exhibit a solvation tendency at least as strong as those in the gas phase and that a balance of interactions between anions, water and metal is achieved at the maximum stabilized water coverage.

Deuterium Exchange Experiments

We observed isotopic exchange in all water desorption states including the multilayer ice state. To quantify the extent of deuterium exchange in the adlayers, an approach to equilibrium in state i , η_i , is defined as:

$$\eta_i = \frac{\theta_i^D / (\theta_i^D + \theta_i^H)}{\sum_i \theta_i^D / \sum_i (\theta_i^D + \theta_i^H)}, \quad (5)$$

where the numerator represents the atom fraction of D in state i and the denominator the atom fraction of D in the entire adlayer. Comparing the two terms above allows us to determine if exchange in the adlayers is complete. Complete exchange for state i occurs when η_i is equal to 1.

The comparison of the approach to equilibrium of the different desorption states as a function of water coverage is shown in Figure 7. The solid circles, open triangles, open squares, and filled diamonds represent the α , β , γ and δ desorption states, respectively. The lines are drawn to guide the eye. The decrease of η_i in the δ state from 1.5 to 1.2 with increasing water coverage suggests incomplete exchange of deuterium *out of* the δ state at low water coverage, but that the exchange approaches completion (equilibrium) when the water coverage increases. On the other hand, the increase of η_i from 0.5 to 1.0 for the α state suggests incomplete exchange of deuterium *into* the α state at low coverage. The exchange is complete only when there is about 2.5 ML of water, thus proving that full water multilayers are necessary to achieve equilibrium exchange. In the β state η_i remains at about 1.0 for almost all H₂O coverages. A dashed line is drawn for the γ state data which are scattered between 1.1 and 1.3 and have no noticeable trend. For the β and

γ states exchange appears to be complete for all water coverages. This observation is consistent with the β and γ state water molecules interacting more directly with the OH groups and therefore acting as intermediates for deuterium exchange from the source (δ state) to the destination (α state).

OH Solvation and Ionization

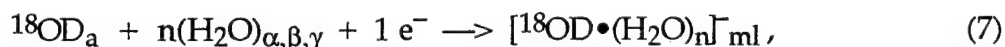
We now consider the behavior of adsorbed OH groups in the OH/H₂O adlayer at a coverage of 0.11 ML of OH groups, which corresponds to the maximum amount of stabilized water. The situation is shown in Figure 6 with the OH groups labeled (a) - (c) and the water molecules labeled (1) - (5). The labeled oxygens are indicated by an asterisk. The γ -state molecules (1,3) are shown in the form of the (OH)₂-H₂O complex and β -state molecules (2,5) interact through one hydrogen bond to the OH groups. α -state molecules (4,6) interact by hydrogen bonding to the β or γ molecules.

Through proton mobility, the structure in this adlayer can transform to that of Figure 6B by virtue of exchange between the β -state molecule (2) and the OH group (b),

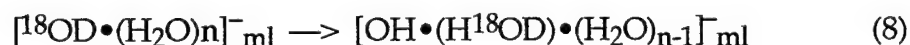


where the ml subscript designates the multilayer phase. The result is an OH⁻ ion now removed from the surface and fully solvated, and a water molecule in direct contact with the surface that may be characterized as β since it is in contact with the OH⁻ group.

Another route for formation of fully solvated OH is by direct migration of the entity away from the surface and into the ice multilayers. Experiments with ^{18}OD allowed this possibility to be examined and the presence of labeled oxygen in the α -state in Figure 4 provides the necessary evidence. These experiments correspond to the case of a full extended surface bilayer, so that α -state molecules must reside in the multilayers; they cannot contact the surface directly. The oxygen label appears in the α -state whenever there is a sufficient amount of excess multilayers to stabilize and solvate a hydroxide ion. Note that the first appearance of the label in the α -state occurs at a water coverage of 1.4 ML, which is enough to fill the extended surface bilayer and just begin to form excess multilayers. The label is especially evident in the α -state when there is greater than one excess multilayer (top curve). This we take as evidence that ^{18}OD "desorbs" from the surface to become a fully hydrated hydroxide ion. This process involves substantial reorganization of a number of molecules and may be written as



Appearance of the ^{18}O label in the α -state can be understood through subsequent conversion to molecular water by proton transfer



followed by thermal desorption of the adlayers



where the gaseous water molecules may appear in the α , β , and γ states and the temperature was assumed to be less than 280 K in equation (9). Equations (7-9) denote a process of combined molecular diffusion (eq. 7) and proton exchange (eqs. 8, 9), processes both known to occur in bulk water ice [38,39]

This process requires the presence of the α -state and therefore may be significant in explaining the previous report of stabilization of molecular oxygen by water on Ag(110) [12]. Because molecular and atomic oxygen co-exist on Ag(110) before 170 K, adsorbed hydroxyl groups formed by reaction (2) are involved in the interaction. Stabilization occurred only in the presence of the α -state, the same condition reported for formation of fully solvated OH^- . Apparently, the solvated hydroxides have some influence on the stability of adsorbed, molecular oxygen, though the exact details remain unclear.

Thermodynamic Feasibility of OH Ionization and Solvation

The Born-Haber analysis of the process, shown in Figure 8, supports the ionization and solvation of OH. The analysis first considers an OH group adsorbed on the Ag(110) surface. The surface OH desorbs into the gas phase with an energy requirement equal to the negative of its heat of adsorption, $-\Delta H_{\text{ads}}$. The work of removing an electron from inside a metal to just outside its surface is defined as the work function [40] and its value for a clean Ag(110) surface is 4.2 eV [41]. The hydroxyl group then combines with the electron to form OH^- in the gas phase; the corresponding electron affinity is 1.8 eV [42]. The gas phase ion is then hydrated by water and gains the heat of hydration, which is estimated to be -5.5 eV [37].

The formation of hydroxyl ion in the water adlayer is thermodynamically favorable only if the free energy change of the overall reaction is less than zero:

$$-\Delta H_{\text{ads}} + \Phi_m - E.A. + \Delta H_{\text{hyd}} \leq 0 \quad (10)$$

Due to the low temperature of this work, we assume that the entropic contribution to free energy is negligible, so the calculated values of enthalpies have been treated as free energies. Solving eqn. (10), we obtain the maximum magnitude for heat of adsorption of surface OH in order for solvation to be feasible, $|\Delta H_{\text{ads}}|_{\text{max}} = 3.1 \text{ eV}$. The heat of adsorption of OH cannot be determined directly by thermal analysis, as surface OH groups decompose to form water and oxygen instead of desorbing molecularly. Using a similar Born-Haber cycle analysis as above, the heat of adsorption has been estimated to be -2.0 eV . This is well below the estimated maximum magnitude, and thus shows that ionization and solvation of OH is feasible on Ag(110).

5. Conclusion

The TPD experiments combined with isotopic exchange have illustrated the necessary evidence for the solvation of hydroxyl group in water adlayers. We obtain a surface solvation number as high as 17 in the limit of zero OH coverage. Water molecules stabilized by the presence of OH are in direct contact with the surface in the form of an extended surface bilayer. The maximum coverage of stabilized water occurred for 0.11 ML of OH, and the maximum adlayer coverage, 1.04 ML, agrees with the bilayer

coverage. On the basis of isotope exchange experiments involving OD and ^{18}OD we showed that hydroxyl groups can ionize to OH^- , desorb from the surface, and become fully solvated in the multilayer phase. The feasibility of this process was confirmed by a Born-Haber analysis. This finding of fully solvated OH^- thus confirms the validity of the UHV-EC analogy for characterizing surface reactions.

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FIGURE CAPTIONS

- Figure 1 TPD spectrum of water following water adsorption at 110 K onto oxygen-covered Ag(110).
- Figure 2 TPD spectra of D₂O for various H₂O coverages on Ag(110) pre-covered with 0.12 ML OD.
- Figure 3 TPD spectra of 0.5 ML H₂O adsorbed on 0.12 ML OD on Ag(110). The thinner line is the D₂O ($m/e = 20$) spectrum and the thicker line is the H₂O ($m/e = 18$) spectrum.
- Figure 4 TPD spectra of HD¹⁸O for various H₂O coverages at 0.03 ML of ¹⁸OD and 0.10 ML OD pre-coverage.
- Figure 5 Surface solvation number N_s and coverage of stabilized water θ_w^s for H₂O/OH/Ag(110) for total water coverages of 1 ~ 2 ML.
- Figure 6 Proposed extended surface bilayer model of the β -state and other water molecules. (A) all OH groups in direct contact with the surface; (B) desorption and solvation of OH⁻ on Ag(110).
- Figure 7 Extent of deuterium exchange η_i as a function of water coverage for an OD coverage of 0.1 ML.
- Figure 8 Born-Haber thermodynamic cycle for surface OH solvation.

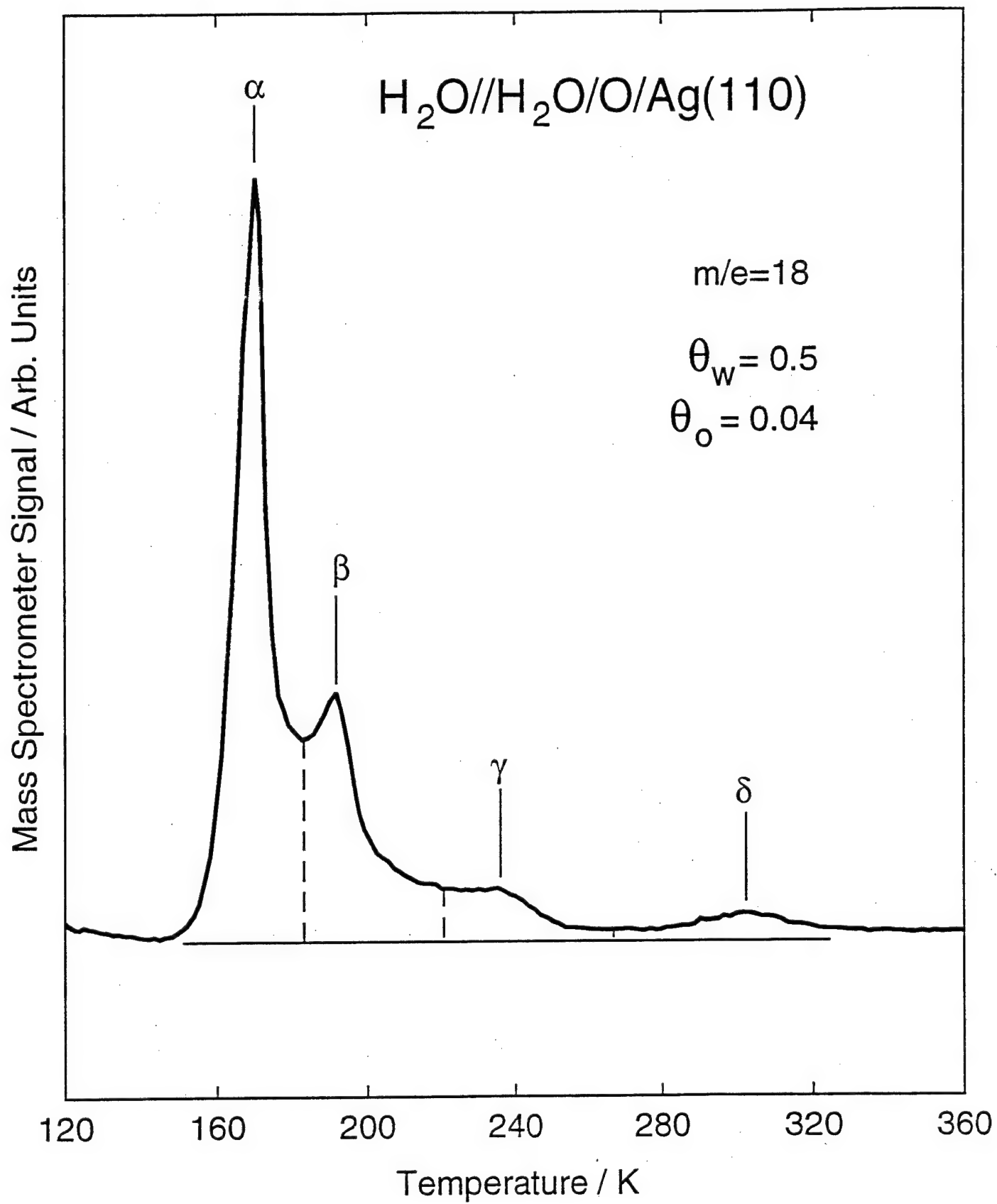


Figure 1, Lim and Stuve

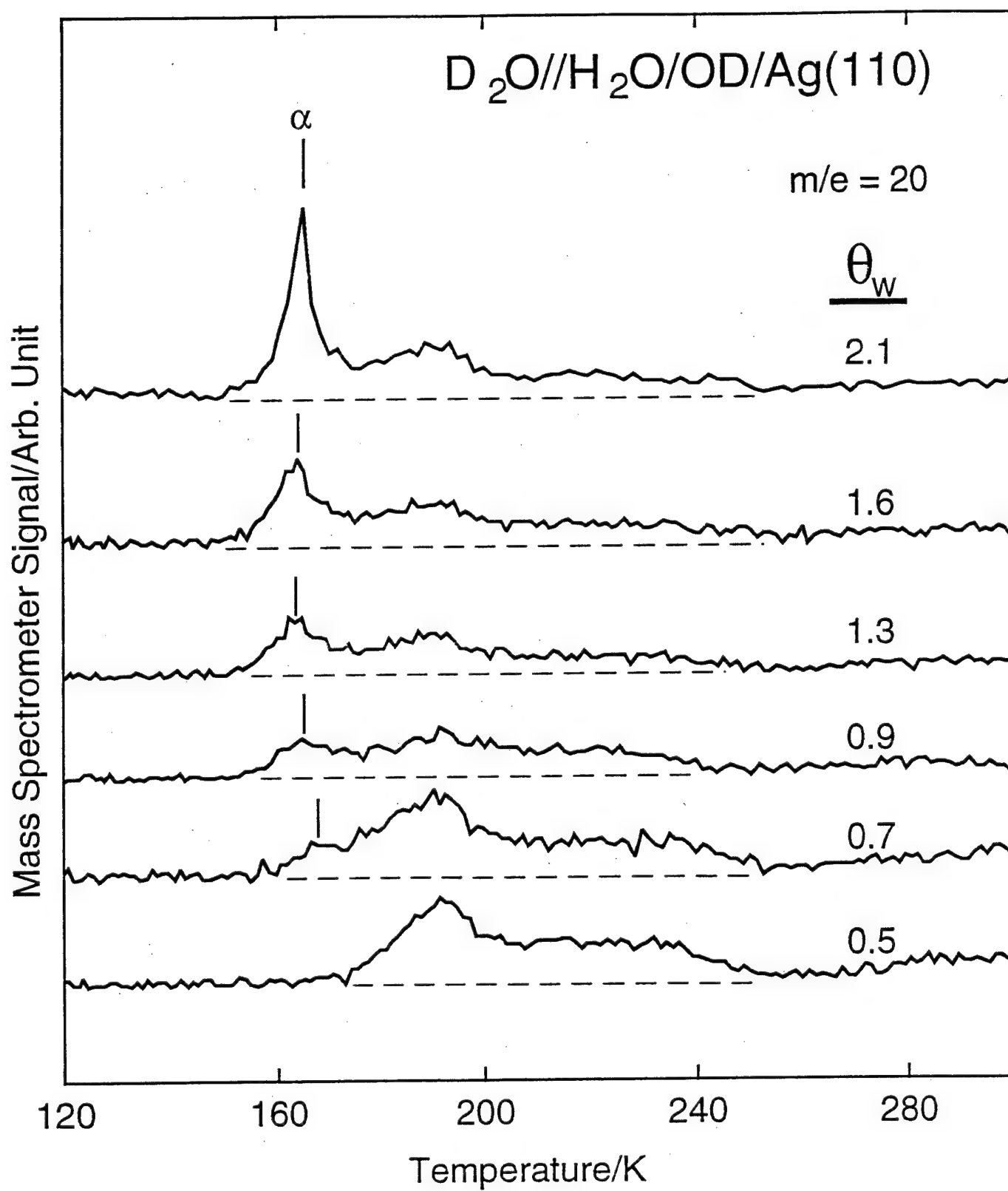


Figure 2, Lim and Stuve

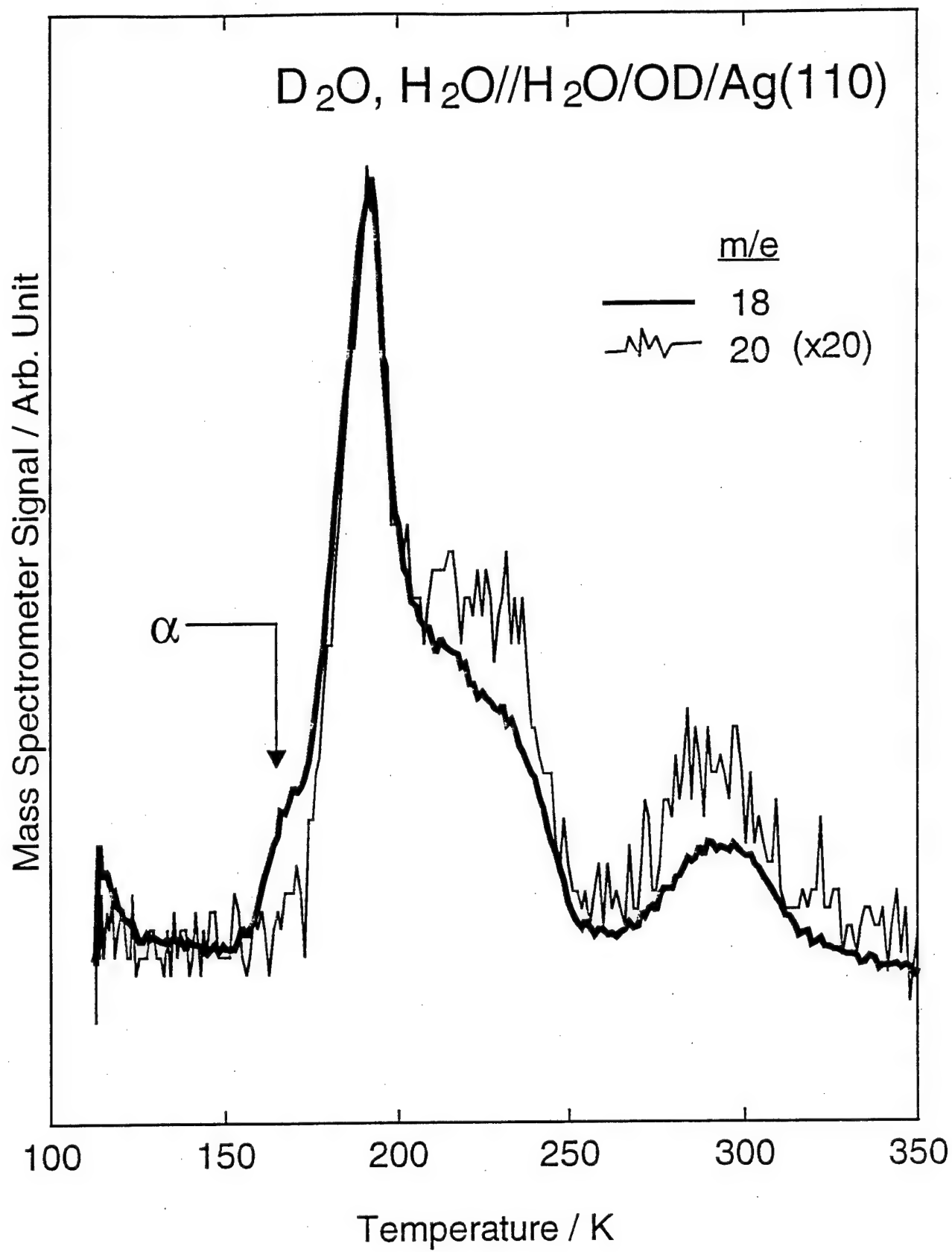


Figure 3, Lim and Stuve

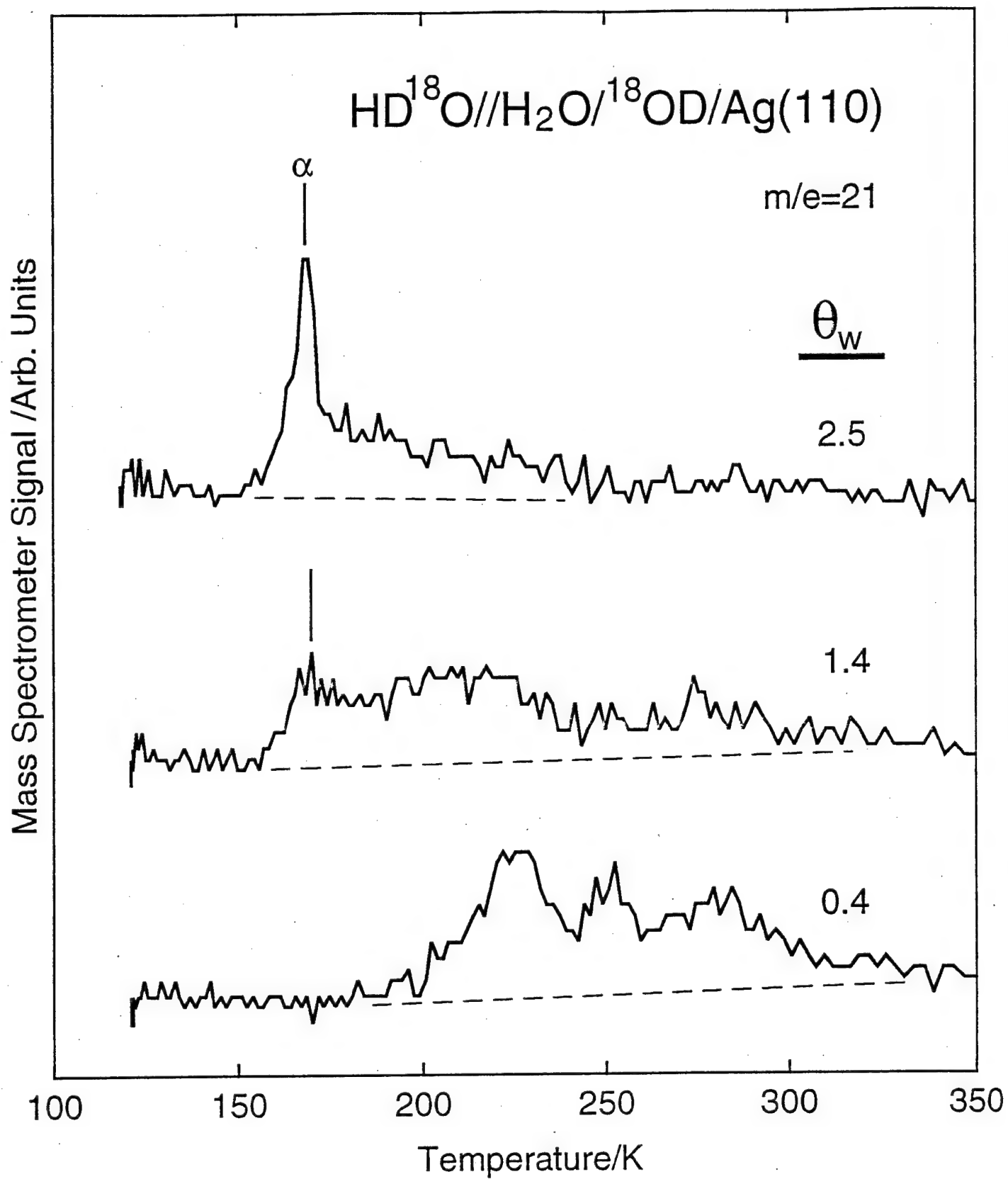


Figure 4, Lim and Stuve

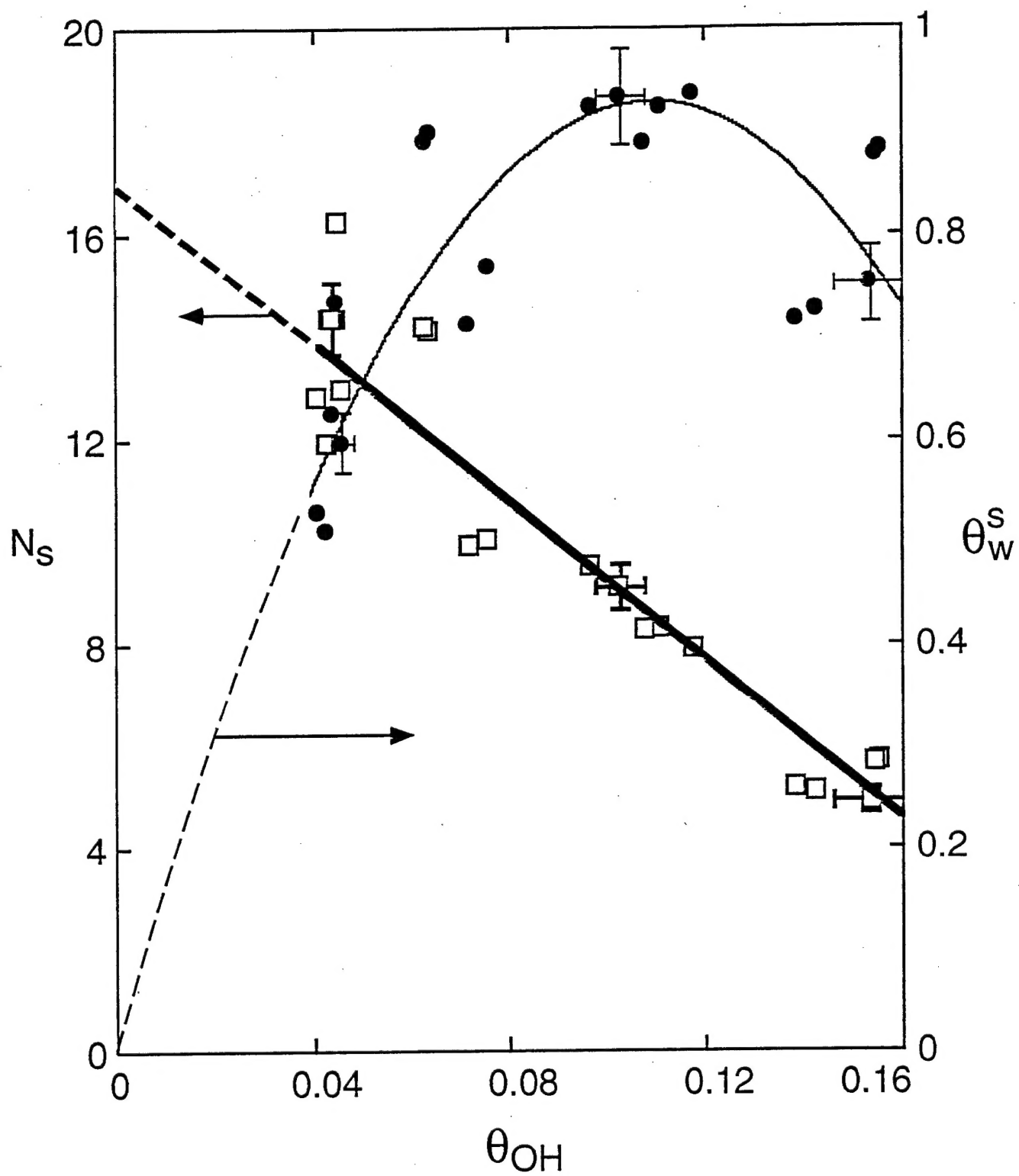


Figure 5, Lim and Stuve

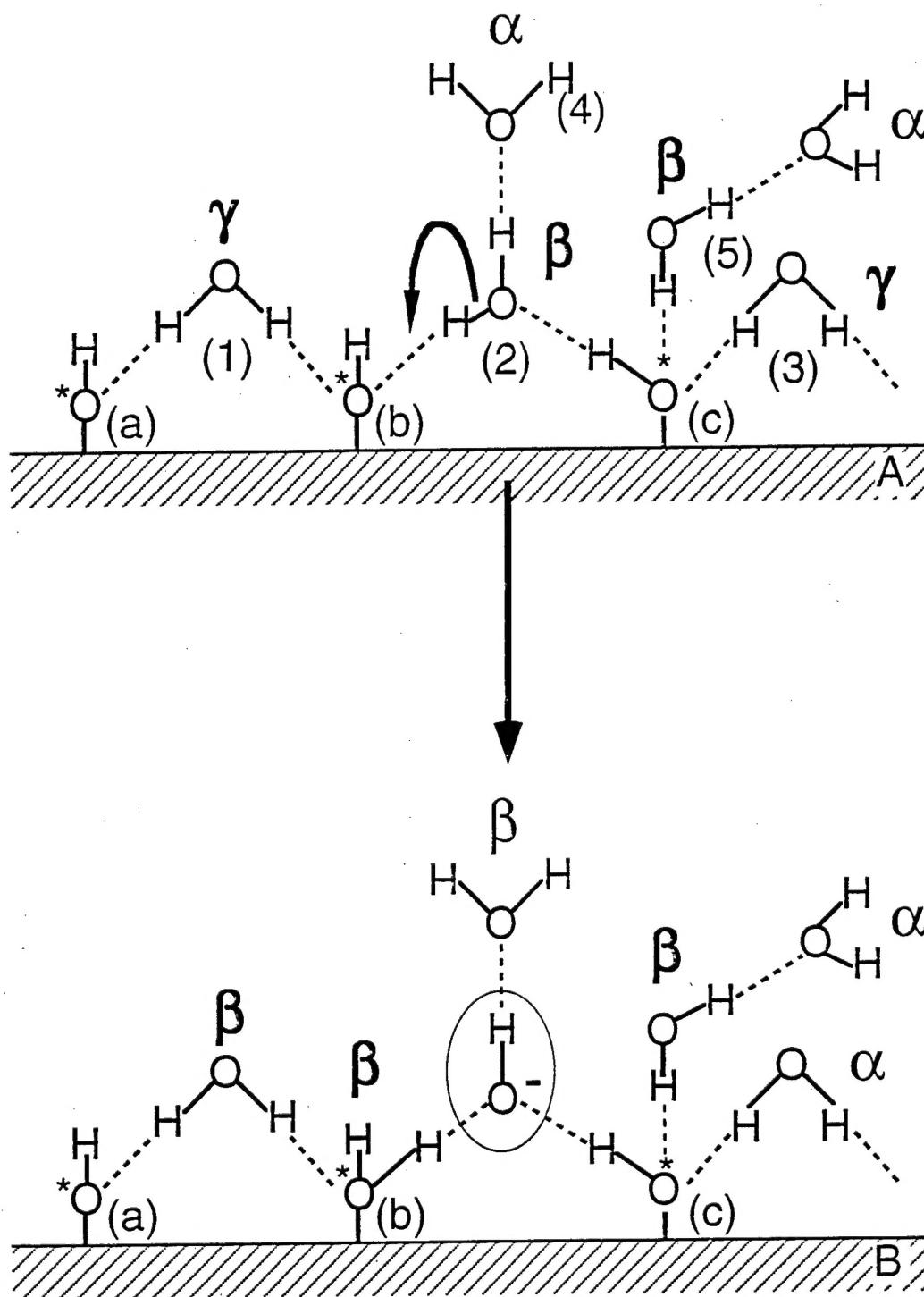


Figure 6, Lim and Stuve

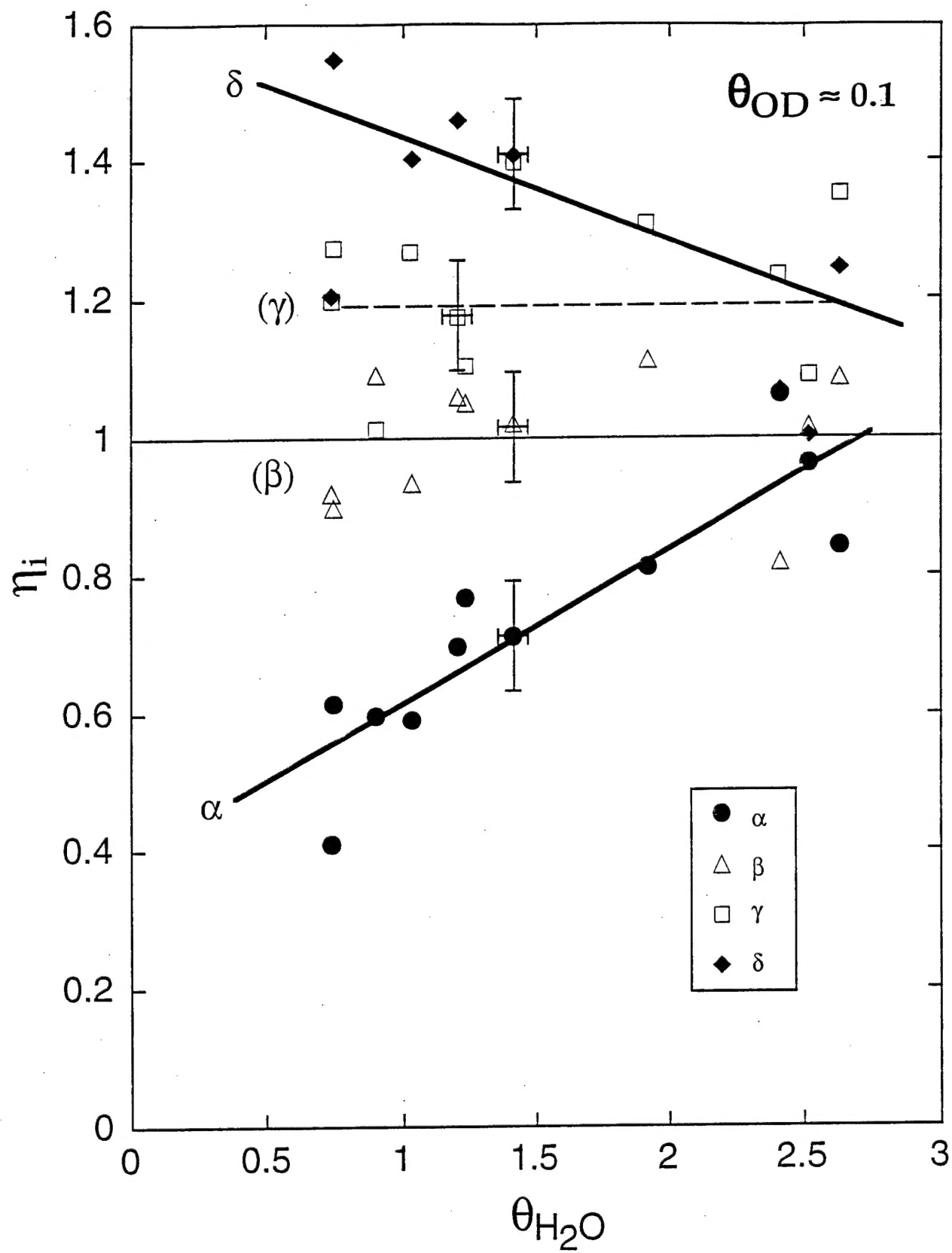
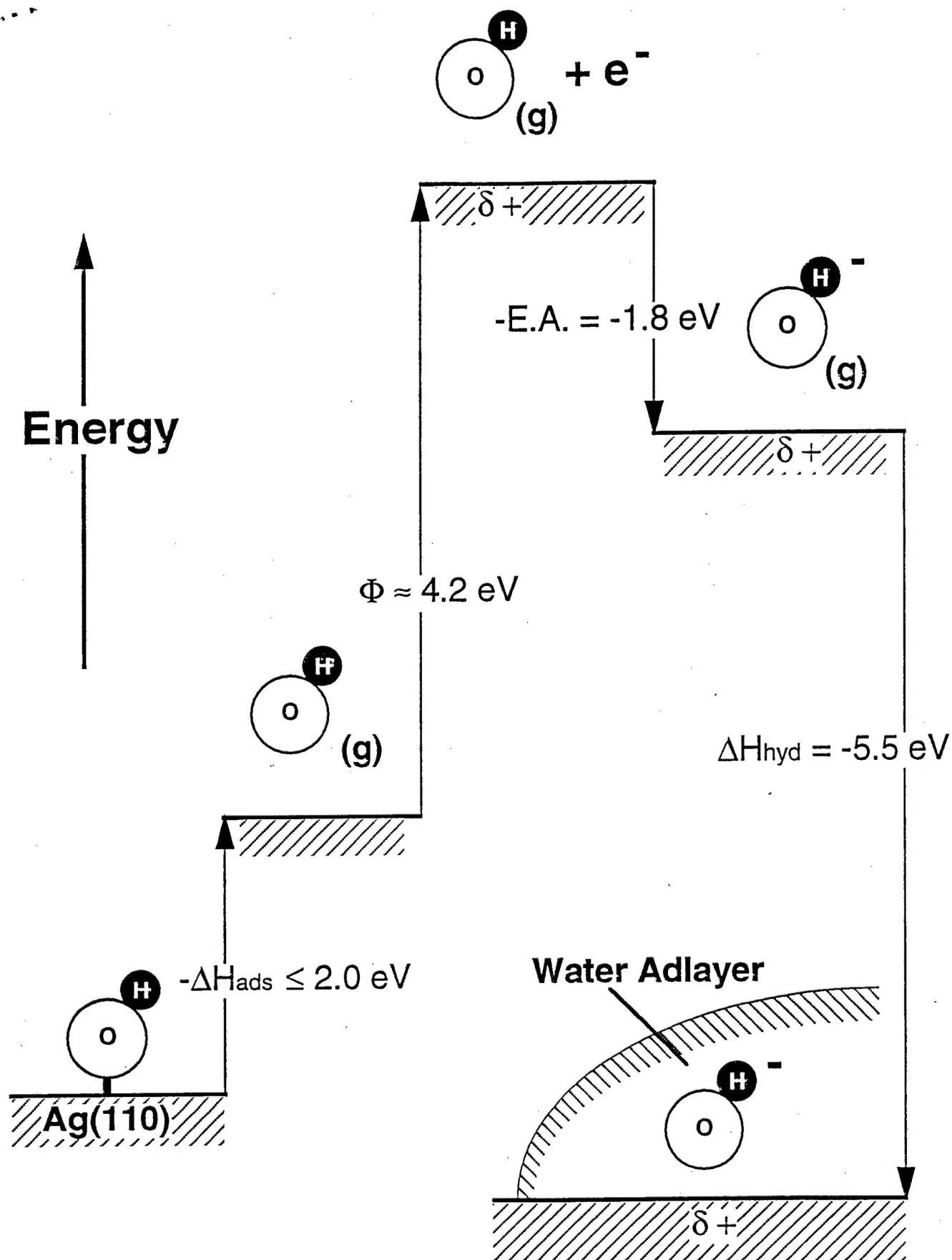


Figure 7, Lim and Stuve



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Figure 8, Lim and Stuve